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<b>(21) International Application Number:</b> PCT/US92/08811 <b>(22) International Filing Date:</b> 22 October 1992 (22.10.92)  <b>(30) Priority data:</b> 3/308227 29 October 1991 (29.10.91) JP  <b>(71) Applicant (for all designated States except US):</b> HENKEL CORPORATION [US/US]; 140 Germantown Pike, Suite 150, Plymouth Meeting, PA 19462 (US).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only) :</b> FURUYAMA, Osamu [JP/JP]; 20-4, Nakao-cho, Asahi-ku, Yokohama-shi, Kanagawa-ken 241 (JP). MORITA, Ryoji [JP/JP]; 3-8-611, Ohara, Hiratsuka-shi, Kanagawa-ken 254 (JP). ISHII, Hitoshi [JP/JP]; 203 Coopo-Ato, 1514-12, Tamura, Hiratsuka-shi, Kanagawa-ken 254 (JP).		<b>(74) Agent:</b> WISDOM, Norvell, E., Jr.; Henkel Corporation, 140 Germantown Pike, Suite 150, Plymouth Meeting, PA 19462 (US).  <b>(81) Designated States:</b> AU, BR, CA, KP, KR, NO, RU, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, SE).  <b>Published</b> <i>With international search report.</i>

**(54) Title:** TREATMENT FOR THE FORMATION OF A CORROSION RESISTANT FILM ON METAL SURFACES**(57) Abstract**

A phosphate surface-treatment bath which contains a cationic organic polymeric compound (or salt thereof) that contains at least one cationic nitrogen atom and has a molecular weight of 1,000 to 1,000,000 forms a highly corrosion resistant film on metal surfaces (e.g., iron, zinc, aluminum, etc.) that is also an excellent paint undercoat. The film preferably is one in which the resin composed of the cationic organic compound (or salt thereof) has penetrated into the grain boundaries between phosphate crystals with an accompanying formation of a phosphate crystal/resin composite. A film formed in accordance with the present invention affords a remarkable improvement in corrosion resistance and paint adherence, compared with the phosphate conversion achieved with the same treatment, except for the omission of the organic polymer containing cationic nitrogen. In addition, even when the primer coating step is omitted, the present invention exhibits a performance approximately equivalent to the application of a primer coating on a conventional phosphate film.

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Description**TREATMENT FOR THE FORMATION OF A CORROSION RESISTANT FILM  
ON METAL SURFACES**Technical Field

The present invention relates to a novel treatment agent that forms a strongly corrosion-resistant film on the surface of metals such as iron, zinc, aluminum, and the like. This film is also an excellent paint undercoat.

Background Art

At present, increasingly high levels of corrosion resistance are being required of painted objects such as automobile bodies and construction materials. Metal surfaces have heretofore been treated by phosphate treatments, chromate treatments, etc.; however, the prior metal surface treatment agents do not always exhibit a satisfactory corrosion resistance and paint adherence.

The art is already familiar with the formation of a phosphate film on a metal surface as a generally applicable pretreatment method when organic films, e.g., paints, adhesives, and the like, are applied on the surfaces of metals such as iron, zinc, aluminum, and the like. The corrosion resistance and paint adherence are improved by this addition of a phosphate film on the metal surface prior to the application of the organic coating (typically paint). When higher levels of corrosion resistance are required, both a phosphate treatment and a post-treatment (e.g., sealing with chromic acid and the like) or primer application are carried out prior to painting. However, these post-treatments (e.g., sealing with chromic acid and the like) contribute only minor benefits. Moreover, while the application of a primer does improve the paintability, this also expands the painting process and thus substantially impairs the workability.

Nevertheless, primer application is currently required for painted objects such as automobile bodies and construc-

tion materials. In the case of automobile bodies, a zinc phosphate film is formed on the metal surface, which is then immersed in aqueous paint for electrodeposition coating. This coating operation is a type of primer coating, and its purpose is to increase the corrosion resistance of the painted surface and to secure corrosion resistance for the interior surfaces of the automobile body, which can be difficult to finish coat. A primer coating is similarly applied on construction materials prior to finish coating in order to increase the corrosion resistance.

While improvements in operating efficiency and cost reduction in painting operations require a contraction of the process, a satisfactory response to this goal has yet to be developed. Thus, phosphate films alone have a poor corrosion resistance, while painting alone does not satisfy the requirements for corrosion resistance and paint adherence. When higher levels of corrosion resistance are required, both a phosphate film and a primer coating are required. This results in high painting costs and requires large work areas. The development of a metal surface treatment agent that exhibits a high corrosion resistance and paint adherence is therefore desired. The development of a metal-surface-treatment agent that permits the omission of primer coating is also desired.

#### Disclosure of the Invention

##### Problems to Be Solved by the Invention

As a means of responding to the above-listed problems, the present invention takes as its object the introduction of a metal-surface-treatment agent that can impart a high corrosion resistance and paint adherence to metals that are suitable for phosphate film treatment, such as iron, zinc, aluminum, and the like (hereinafter briefly denoted simply as "metal"). A further object of the present invention is the introduction of a metal surface treatment agent that permits the omission of primer coating while at the same time retaining the level of corrosion resistance currently available.

Summary of the Invention

As the result of extensive research directed at solving the aforementioned problems, it has now been discovered that a high corrosion resistance and paint adherence are obtained by film formation from a phosphate treatment bath that contains an organic polymeric compound (or salt thereof) having certain properties. The present invention was developed as a result of this discovery.

That is, a film that exhibits the highly desirable properties specified above can be formed by treating the metal surface with a treatment agent for the formation of a film on metal surfaces, wherein said treatment agent characteristically comprises a phosphate surface treatment bath which contains a cationic organic polymeric compound (or salt thereof) that contains at least 1 cationic nitrogen atom and has a molecular weight of 1,000 to 1,000,000. The film according to the present invention preferably is a composite film in which the resin composed of the cationic organic compound (or salt thereof) has penetrated into the grain boundaries between phosphate crystals with an accompanying formation of a phosphate crystal/resin composite.

The surface treatment agent according to the present invention comprises the solution or stable dispersion of a cationic organic polymeric compound (or salt thereof) in a phosphate treatment bath. Said phosphate treatment bath comprises any surface-treatment bath that is capable of forming a phosphate film on the surface of a metal such as iron, zinc, aluminum, etc., either for a single species of metal alone or simultaneously on the surfaces of two or more species of the preceding metals. In general, its essential components are zinc ions and phosphate ions, but it may optionally contain nitrate ions, other metal ions (nickel, manganese, calcium, and the like), fluoride, and various types of oxidants. However, the phosphate treatment bath is not specifically restricted within the context of the present invention, and the present invention encom-

passes all known phosphate treatment baths.

5 The cationic organic polymeric compound should contain at least 1 cationic nitrogen atom and should have a molecular weight of 1,000 to 1,000,000. Although its structure is not restricted in the broadest embodiments of the invention, organic polymers are particularly preferred that have a resin skeleton comprising at least one selection from epoxy resins, urethane resins, polybutadiene resins, acrylic resins, and maleic anhydride resins, wherein these  
10 resins contain a cationic nitrogen-containing group.

The salts of the cationic organic polymeric compound encompass its inorganic salts and organic salts. The inorganic salts are exemplified by phosphate, nitrate, sulfate, and the like, and the organic salts are exemplified by acetate, propionate, glyconate, and the like. A single species or two or more species of this cationic organic polymeric compound (or salt thereof) can be employed. Only a weak improvement in corrosion resistance is obtained at molecular weights below 1,000, while it is very difficult  
15 to obtain dissolution or stable dispersion in zinc phosphate baths at molecular weights in excess of 1,000,000.  
20

Moreover, paint additives (such as pigment and the like), other types of resins, activators, and the like may be added on an optional basis.

25 With respect to the technique for treating the metal surface, the present invention can employ conversion treatment by spray or immersion as well as electrolytic methodologies, and the treatment agent according to the present invention is not limited to a particular treatment method.

30

#### Examples

The effects of the present invention will be explained in detail in the following using illustrative examples and comparison examples; however, the present invention is not limited to the examples, which describe merely a typical  
35 pre-paint phosphate treatment and a typical painting system. In comparison examples, evaluation and treatment were conducted as in the examples, but with the use of organic

polymeric compound outside the scope of the present invention and with omission of the cationic organic polymer altogether.

The general conditions for the examples and comparison examples were as follows:

Workpieces: Cold-rolled steel sheet; electroplated steel sheet (zinc coating = 20 g/m<sup>2</sup>); aluminum sheet (JIS 5052).  
Surface treatment agents: The cationic organic polymeric compounds used in the examples and the polymeric compounds used in the comparison examples are reported in Table 1. PARBOND<sup>TM</sup> L3020 (surface-treatment agent for automotive applications from Nihon Parkerizing Company, Limited) was used for the organic polymer-free phosphate surface treatment bath. This was a typical phosphate surface-treatment bath.

Treatment sequence:

- 1) Degreasing: 2 % solution of FINECLEANER<sup>TM</sup> L4460 (from Nihon Parkerizing Company, Ltd.), 120 second spray at 42° C
- 2) Water wash: 30 second spray at room temperature
- 3) Surface conditioning: 0.1 % solution of PARCOLENE<sup>TM</sup> ZN (from Nihon Parkerizing Company, Ltd.), 20 second spray at room temperature
- 4) The surface-treatment agents according to the present invention and the surface-treatment agents in the comparison examples were both applied under the following conditions: immersion at 42° C for 120 seconds.
- 5) Water wash: 30 second spray at room temperature
- 6) Wash with deionized water (conductivity, 0.2 microsiemens/cm): 20 second spray at room temperature

After completion of the six process steps noted above and drying, painting was conducted by the following processes (the primer step was sometimes omitted, as noted in the tables below):

Table 1

Designation of Treatment	Chemical Nature of the Organic Polymeric Compound Used	Molecular Weight
A	adduct of $\text{HN}(\text{CH}_3)_2$ with bisphenol A epoxy resin	8,800
B	copolymer of methyl methacrylate and dimethylaminoethyl methacrylate	20,000
C	adduct of $\text{H}_2\text{NCH}_2\text{N}(\text{CH}_3)_2$ with maleic anhydride resin	2,000
a	adduct of $\text{H}_2\text{NCH}_2\text{N}(\text{CH}_3)_2$ with maleic maleic anhydride resin	800
b	polyvinyl alcohol	3,000

- 1) Primer coating: Electrodeposition painting with ELE-CRON<sup>TM</sup> 9410 from Kansai Paint Kabushiki Kaisha to produce a film thickness = 20 micrometers; baking at 175° C for 30 minutes
- 2) Intermediate coating: KPX36 from Kansai Paint Kabushiki Kaisha; film thickness = 30 micrometers; baking at 140° C for 30 minutes
- 3) Finish coating: RUGABAKE<sup>TM</sup> B 531 from Kansai Paint Kabushiki Kaisha; film thickness 40 micrometers; baking at 140° C for 30 minutes.

All the process steps noted above were carried out in the same manner for both the examples and the comparison examples, except for the chemical nature of the surface-treatment agents used (in step 4).

#### Performance evaluation:

- 1) Water-resistant secondary adhesion: The painted sheet was immersed in deionized water at 40° C for 240 hours, and a checkerboard of 100 squares (2 mm x 2 mm) was scribed into the base material using a sharp cutter. After peeling with cellophane tape, the number of peeled squares was counted. A smaller number of peeled squares indicates a better score.
- 2) Composite cycle test: A cross was scribed in the painted sheet through to the base material, using a



sharp cutter, and the painted sheet was then subjected to 14 repetitions of the  $T_1 \rightarrow T_2$  cycle (see below). After the test, evaluation was carried out by measuring the maximum one side film blister width from the inscribed cross.

$T_1$  : salt-spray test (JIS Z 2371) : 24 hours  
 $T_2$  : wetting test (50° C, 70 % RH) : 216 hours

#### Benefits of the Invention

Tables 2, 3, and 4 report the paint adherence and corrosion resistance of the films obtained by surface treatment, respectively, of cold-rolled steel sheet, electrogalvanized steel sheet, and aluminum sheet. These tables also include the results for the comparison examples.

In the case of treatment by a metal-surface-treatment agent for composite film formation in accordance with the present invention, the results confirm a remarkable improvement in corrosion resistance and paint adherence over phosphate treatment. In addition, even with omission of primer coating, the present invention exhibits a performance approximately equivalent to the application of a primer coat on phosphate film.

When an organic polymeric compound was used that was not within the scope of the present invention, either substantially no effect was obtained or the performance was in fact degraded.

As discussed hereinbefore, the metal surface treatment agent for composite film formation in accordance with the invention increases the corrosion resistance and paint adherence and makes possible the omission of primer coating.

Table 2					
Example ("Ex") or Com- parison Example ("CE") Number	Organic Polymer Component		Primer Coating Used?	Water Resist- ant Secon- dary Adhe- sion: Number Peeled	Compos- ite Cycle Test: Blister Width in mm
	Type	Concen- tration			
Ex 1	A	0.1 %	yes	0	$\leq 0.5$
Ex 2	B	0.5 %	yes	0	$\leq 0.5$
Ex 3	C	2.0 %	yes	0	$\leq 0.5$
Ex 4	A	1.0 %	no	0	1.7
CE 1	none		yes	0	1.5
CE 2	none		no	57	4.4
CE 3	a	1.0 %	yes	0	1.4
CE 4	b	1.0 %	yes	37	1.7

Table 3					
Example ("Ex") or Com- parison Example ("CE") Number	Organic Polymer Component		Primer Coating Used?	Water Resist- ant Secon- dary Adhe- sion: Number Peeled	Compos- ite Cycle Test: Blister Width in mm
	Type	Concen- tration			
Ex 5	A	0.1 %	yes	0	$\leq 0.5$
Ex 6	B	0.5 %	yes	0	$\leq 0.5$
Ex 7	C	2.0 %	yes	0	$\leq 0.5$
Ex 8	A	1.0 %	no	0	1.2
CE 5	none		yes	0	1.0
CE 6	none		no	36	2.2
CE 7	a	1.0 %	yes	0	1.1
CE 8	b	1.0 %	yes	17	1.8

Table 4					
Example ("Ex") or Com- parison Example ("CE") Number	Organic Polymer Component		Primer Coating Used?	Water Resist- ant Sec- ondary Adhe- sion: Number Peeled	Compos- ite Cycle Test: Blister Width in mm
	Type	Concen- tration			
Ex 9	A	0.1 %	yes	0	≤ 0.5
Ex 10	B	0.5 %	yes	0	≤ 0.5
Ex 11	C	2.0 %	yes	0	≤ 0.5
Ex 12	A	1.0 %	no	6	0.7
CE 9	none		yes	5	0.8
CE 10	none		no	36	1.5
CE 11	a	1.0 %	yes	4	0.8
CE 12	b	1.0 %	yes	17	1.2

Claims

1. A phosphate conversion coating treatment composition for metal surfaces, characterized in that the treatment composition comprises a cationic organic polymeric compound that contains at least 1 cationic nitrogen atom and has a molecular weight of 1,000 to 1,000,000, or a salt of such a cationic organic polymeric compound.
2. A phosphate conversion coating treatment according to claim 1, wherein the cationic organic polymeric compound is a compound having a resin skeleton comprising at least one selection from epoxy resins, urethane resins, polybutadiene resins, acrylic resins, and maleic anhydride resins.
3. A process for forming a protective coating on a metal by contacting the metal with a phosphate conversion coating solution, characterized in that the phosphate conversion coating solution has a composition according to claim 1 or 2.
4. A process according to claim 3, wherein the metal is iron, zinc, or aluminum.
5. A process according to claim 4, wherein the protective coating formed has a composite structure, in which the resin containing the cationic organic compound or salt thereof penetrates into grain boundaries between phosphate crystals.
6. An article of manufacture comprising an outer surface of an organic protective coating, an intermediate film including phosphate ions underlying the organic protective coating, and a metal underlying the intermediate coating, characterized in that the intermediate coating has a composite structure, in which a resin containing a cationic nitrogen containing organic polymer or a salt thereof penetrates into grain boundaries between phosphate crystals.

# INTERNATIONAL SEARCH REPORT

International Application No PCT/US 92/08811

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl.5                      C 23 C 22/33                      C 23 C 22/07                      C 23 C 22/12 C 23 C 22/28		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.Cl.5	C 23 C                      C 23 F	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	DE,A,3900149 (KAO CORP.) 13 July 1989, see pages 11-12,23 -----	1-4
X	EP,A,0160505 (DEARBORN CHEMICALS LTD) 6 November 1985, see page 2, lines 12-28; page 4, line 13 - page 8, line 12 -----	1-4
A	EP,A,0385251 (HENKEL KG AUF AKTIEN) 5 September 1990 -----	1-4
A,P	WO,A,9209721 (HENKEL CORP.) 11 June 1992 -----	1-4
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p><sup>10</sup> Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p> </div> </div>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
14-01-1993		02 FEB 1993
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EUROPEAN PATENT OFFICE		BRITT-MARIE LUNDELL

# ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

US 9208811  
SA 66015

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.  
The members are as contained in the European Patent Office EDP file on 27/01/93  
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